

REMARKS

Claims 1-3, 8-9, 11 and 15-19 are pending in this application. By this Amendment, claims 4-5, 7, 10, and 12 are canceled and claims 15-19 are added. The specification, at least at page 7, lines 23-26, and page 12, lines 1-6, and the original claims as filed, support new claims 15-19. Thus, no new matter is added. In view of the following remarks, reconsideration and allowance are respectfully requested.

I. Rejection under §103

A. Claims 1-5, 7-8, 10-12 and 14

The June 6, 2003 Office Action and September 12, 2003 Advisory Action rejects claims 1-5, 7-8, 10-12 and 14 under 35 U.S.C. §103(a) over U.S. Patent No. 5,876,684 to Withers et al. ("Withers") in view of JP 11116218 to Chiharu et al. ("Chiharu"). Applicants respectfully traverse the rejection for at least the following reasons.

Claims 4-7, 10 and 12-14 are canceled, thus rendering moot their rejection. Independent claim 1 is directed to methods of manufacturing single-walled carbon nanotubes. The method utilizes an arc discharge and a carboniferous liquid state material under a pressure of at least 39.9 kPa. The claimed method of generating single-walled carbon nanotubes further uses a carboniferous liquid state material comprising a metallic catalyst. Withers and Chiharu do not teach or suggest these methods.

Withers describes a method for synthesizing fullerenes from a liquid hydrocarbon source using a heat-generating process, such as an electrode arc or plasma. The Office Action acknowledges that Withers' method does not utilize the specifically claimed pressure range. However, the Office Action takes the position that selection of the claimed "at least 39.9 kPa" is the mere "optimization of a known process which could have been determined through routine experimentation." Applicants respectfully disagree with this position.

The Advisory Action states that Applicants provide no evidence of unexpected results. In response, Applicants herewith provide evidence to show that the synthesis of carbon nanotubes, using a method within the scope of the claims, produces a dramatically increased nanotube yield that one of ordinary skill in the art would not have expected based upon the teachings of the prior art. Applicants herewith submit a peer-reviewed published manuscript, "New synthesis of multi-walled carbon nanotubes using an arc discharge technique under organic molecular atmospheres," Appl. Phys. A., 73: 451-454 (2001), by Shimotani et al. ("Shimotani"). Shimotani examined nanotube synthesis under various organic atmospheres at different pressures, using methods falling within the scope of the instant claims (page 452, col. 2, first full paragraph). As shown in Figure 4 (page 453), nanotube yield dramatically increased as the pressure increased from 200 to 300 torr. As the pressure further increased, nanotube yield continued to increase, leveling-off at a pressure of about 400-500 torr.

Withers reportedly attempts to maximize fullerene production (col. 2, lines 28-32). In particular, Withers applies various pressure and temperature controls and conditions "that are known to stimulate . . . and maximize the formation of fullerenes of various molecular weights and structures." (col. 2, lines 45-50). From this "shotgun" approach, Withers ultimately describes potential atmospheric conditions of 10^{-6} to 760 torr, an incredible range stretching over about 9 logs (see, e.g. col. 4, lines 63-66). However, in no way does Withers teach or suggest anything that would have motivated one of ordinary skill in the art to conduct nanotube synthesis at a pressure range of at least about 39.9 kPa (about 300 torr), or the much narrower range of 39.9 kPa to 79.8 kPa (300 to 600 torr), as claimed.

Moreover, Withers teaches away from the claimed pressure range. For example, Withers teaches a preference for using a pressure of 100-200 torr. (see, e.g., col. 6, line 15; col. 9, line 23; col. 9, line 55; col. 10, line 47). Withers also teaches that much lower

pressures, in the range of 10^{-3} to 10^{-6} torr can also be used with "attendant advantages." (col. 9, lines 5-10).

As illustrated in Shimotani, nanotube synthesis at 100-200 torr, the range preferred in Withers, provides a yield falling far below that produced under the claimed conditions of at least 39.9 kPa (about 300 torr). Withers does not include anything that would have taught or suggested to one of ordinary skill in the art that further raising the pressure above the preferred 100-200 torr would increase the production of nanotubes. Thus, Withers does not teach manufacturing carbon nanotubes using a system that supplies a carboniferous liquid state material to raise the pressure inside the system to at least 39.9 kPa as claimed.

Chiharu fails to remedy the deficiencies of Withers. Chiharu fails to teach or suggest any particular pressure conditions. In fact, the methods taught by Chiharu are completely silent as to the use of pressure. In no way does Chiharu teach or suggest the production of carbon nanotubes at a pressure of at least 39.9 kPa as claimed. For at least these reasons, Withers and Chiharu, alone or in combination, would not have rendered obvious claims 1-3, 8-9 and 11. For similar reasons, new claims 15-19 would also not have been obvious.

B. Claims 9 and 13

The Office Action rejects claims 9 and 13 under 35 U.S.C. §103(a) over Withers and Chiharu, further in view of Journet et al. ("Journet"). Applicants respectfully traverse the rejection.

Claim 9 depends from claim 1 and features yttrium as the metallic catalyst; claim 13 is canceled. The Office Action relies on Journet to teach the use of yttrium catalysts for increased yield of single-walled carbon nanotubes. However, Journet does not remedy the deficiencies of Withers and Chiharu detailed above. In particular, Journet does not teach or suggest manufacturing carbon nanotubes using a system that supplies a carboniferous liquid

state material to raise the pressure inside the system to at least 39.9 kPa as claimed. Thus, the combination of Withers, Chiharu and Journet would not have rendered obvious claim 9.

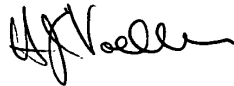
Accordingly, Applicants respectfully request reconsideration and withdrawal of the rejection.

II. Conclusion

In view of the foregoing, it is respectfully submitted that this application is in condition for allowance. Favorable reconsideration and prompt allowance of claims 1-3, 8-9, 11 and 15-19 are earnestly solicited.

Should the Examiner believe that anything further would be desirable in order to place this application in even better condition for allowance, the Examiner is invited to contact the undersigned at the telephone number set forth below.

Respectfully submitted,



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Enclosures:

Shimotani et al: Appl. Phys. A., 73: 451-454 (2001)

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New synthesis of multi-walled carbon nanotubes using an arc discharge technique under organic molecular atmospheres

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Abstract. We have synthesized multi-walled carbon nanotubes (MWNTs) using a DC arc discharge method under organic molecular atmospheres. This method allows us to synthesize about five times more MWNTs than are synthesized using the usual arc discharge method, using discharge conditions of 100 A and 20 V. We have examined the synthetic yield of MWNTs at various pressures under different organic atmospheres. The yield of MWNTs increases with the number of carbon atoms in the organic molecule.

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There has been interest in carbon nanotubes (CNTs) since this material was discovered in 1991 [1]. Many applications for CNTs, such as electronic devices [2, 3], hydrogen storage [4], probe tips for scanning probe microscopes (SPM) [5, 6], field emitters [7], and manipulators for nanotechnology [8] have been proposed because the material has remarkable physical properties [9–12]. Therefore, it is indispensable to establish an efficient method of synthesizing CNTs for such devices.

CNT has been synthesized by various techniques in order to understand its physical properties and growth mechanism [13], including arc discharge [14], laser ablation [15], and chemical vapor deposition (CVD) [16, 17]. The arc discharge process can synthesize 1 g of carbon products, including CNT, per minute [18], and laser ablation can produce products at up to 10 g per day [19]. In comparison, the CVD process can provide well-aligned CNT [20]. However, these methods cannot synthesize sufficient quantities of CNT with sufficient purity at low cost. Therefore, there exists a need for a new synthesis method for CNT.

Among the various synthetic methods for CNT, the arc discharge method is one of the most favorable techniques in terms of efficiency, because CNT can easily grow in a low-energy arc plasma. In this case, the synthesis yield would be controlled by many parameters such as current, voltage drop, and type of atmosphere. Therefore, we can expect that the arc

discharge method would be made more efficient by controlling such parameters precisely. Among such parameters, the CNT yield would be more sensitive to the discharge atmosphere when using the arc discharge method [21]. Furthermore, the atmosphere can be easily controlled. Consequently, we attempted to synthesize CNT using an arc discharge method under various carbonous atmospheres to obtain an efficient low-cost method for synthesizing high-purity CNT.

1 Experimental procedure

We synthesized MWNTs using DC arc discharge under atmospheres of helium (He), ethanol (C_2H_5OH), acetone (CH_3COCH_3) and hexane (C_6H_{14}), at various pressures (from 150 Torr to 500 Torr). Following an oxygen purge, we introduced the organic molecules into the reaction chamber at a known pressure. The cathode and the anode were pure graphite rods. The anode could be moved by a translation mechanism to adjust the distance between the anode and cathode. The typical current and voltage drop of the arc discharge between two electrodes were 100 A and 20 V. The duration of the discharge was ~ 2 min. During the discharge, we adjusted the distance between two electrodes to keep it constant at ~ 3 mm. We generated an arc plasma at various current and voltage conditions. However, we could keep the discharge stable only at the current and voltage conditions of 100 A and 20 V, allowing the efficient synthesis of carbon deposits.

Carbon products on the cathode surface were observed using scanning electron microscopy (SEM, Hitachi S-4500) and transmission electron microscopy (TEM, Hitachi H-9000). We also measured the weight of the carbon deposits to examine the yield of MWNTs under various organic atmospheres at different pressures.

2 Results and discussion

Firstly, we synthesized MWNTs using DC arc discharge for 1 min in He and acetone atmospheres at 500 Torr. The discharging produced a cake-shaped carbon deposit on the cath-

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ode surface in both cases. In the case of discharging in the He atmosphere, the diameter and height of the cake were ~ 8 mm and ~ 7 mm, respectively. In comparison, the discharge under the acetone atmosphere produced a carbon cake deposit of ~ 12 mm in diameter and ~ 15 mm in height. Furthermore, the weight of the cake produced per min was 0.4 g in the He atmosphere and 2.1 g in the acetone atmosphere. Discharging under the acetone atmosphere produced a carbon deposit about five times larger in volume and weight than that produced under the He atmosphere.

The carbon cake deposits consisted of a collar and a cylindrical core. CNTs were observed in the core of the cakes but not in the collar. Figure 1 shows the SEM images of the core of the cakes synthesized in an acetone atmosphere at a pressure of 500 Torr. The images show that there are nanoparticles besides CNTs in the core. Under ethanol and hexane atmospheres, CNTs were also synthesized at the core.

Figure 2 shows a typical TEM image of MWNTs synthesized in an acetone atmosphere at 500 Torr. The image indicates that the CNTs synthesized are MWNTs. Their inner diameter is ~ 3 nm, and their outer diameter is approximately 10–30 nm. DC arc discharge under the He, ethanol and hexane atmospheres also synthesized MWNTs. Upon changing the atmospheres, we found that there was no sig-



Fig. 2. TEM image of typical CNT synthesized in an acetone atmosphere at 500 Torr

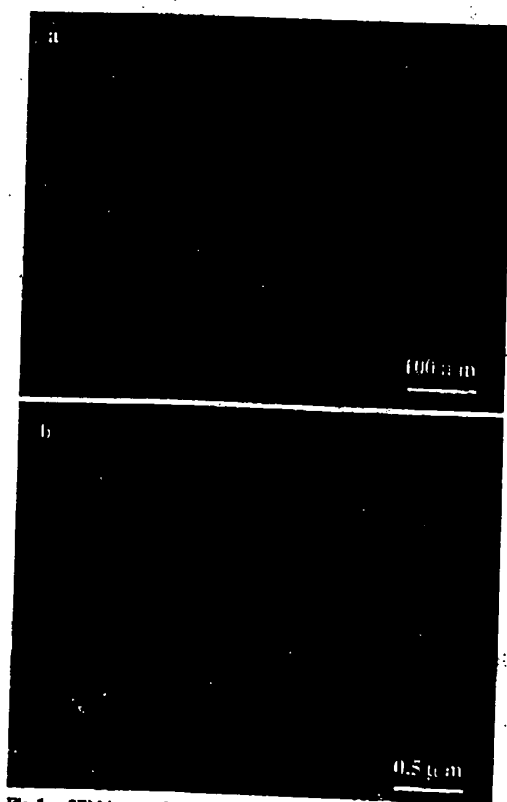


Fig. 1. a SEM image of a carbon cake core synthesized in an acetone atmosphere at 500 Torr. b High-magnification SEM image of a carbon cake core synthesized in an acetone atmosphere at 500 Torr

nificant difference in MWNT character such as diameter and length. However, more carbon deposits were produced under the three organic molecular atmospheres than under the He atmosphere.

We have examined the yield of MWNTs under various organic atmospheres at different pressures. Firstly, we measured the weights of the total carbon deposit (W_t) and the core part (W_c) alone, since MWNTs were observed at the core. In the case of the He atmosphere at 500 Torr, the ratio W_c/W_t was 0.68. In comparison, the ratios in the case of acetone were ~ 0.70 for various pressures. Thus, we can assume that the ratio is constant at 0.70 for all the atmospheres at all pressures. Secondly, we estimated the content of MWNTs in the core using SEM images. Figure 3 shows typical SEM images of the core synthesized in He, ethanol and hexane atmospheres. We estimated the areal ratio (S) of MWNTs from SEM images, which discriminated between MWNTs and nanoparticles. Next, we approximated the volume content of MWNTs as $S^{3/2}$. Using this procedure, the content of MWNTs in all cases were estimated to be approximately 60%–70% of the core volume. This means that the MWNT purity in the core would be constant at $\sim 70\%$, within 10%. Therefore we estimated the yield of MWNTs as half of the total weight of carbon deposit (70% of W_c/W_t).

Figure 4 shows the pressure dependence of the yield of MWNTs for He, acetone, ethanol and hexane atmospheres. Firstly, Figure 4 shows that arc discharges in the three organic atmospheres produce more MWNTs, by two times at least, than those in the He atmosphere. Secondly, in all the cases of organic molecular atmospheres, yields of their MWNTs increase as the pressure increases up to ~ 400 Torr. The yields then tend to saturate. In comparison, in the case of the He atmosphere, the yield of MWNTs is independent of the pressure. Thirdly, under hexane and acetone atmospheres, the MWNTs produced are 2 and 1.5 times larger in weight than those produced under the ethanol atmosphere.

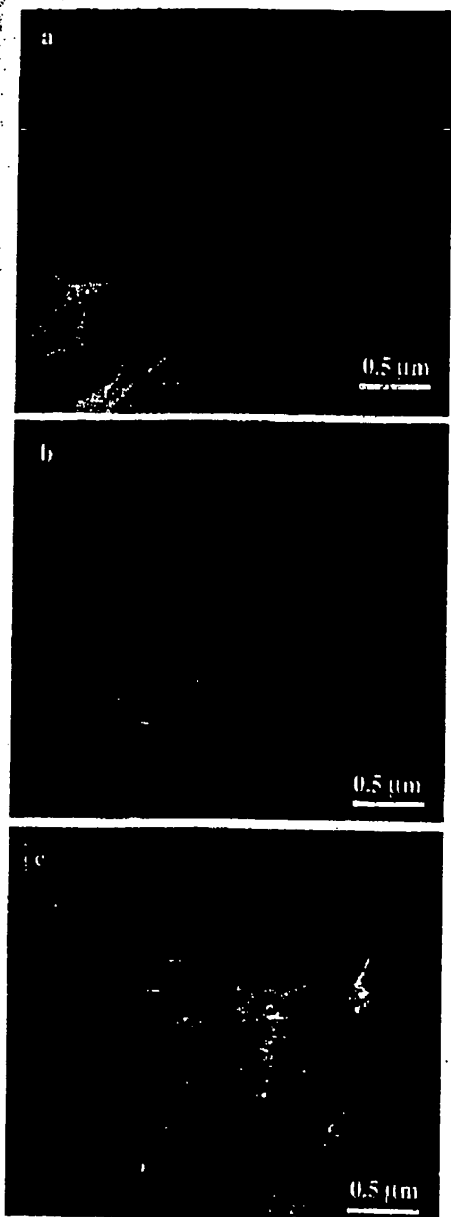


Fig. 3a-c. High-magnification SEM image of a carbon cake core synthesized in He (a) and ethanol (b) at 500 Torr, and hexane atmosphere at 400 Torr (c)

Furthermore, we have examined the synthesis of CNT using arc discharges between tungsten electrodes under an acetone atmosphere. We have confirmed that MWNTs can be synthesized under these conditions. This result shows that acetone is the carbon source for CNT synthesis. Therefore, we can conclude that the ambient carbons, which originate from the organic molecules, act as a source of further carbon during the arc discharge.

Under the acetone, ethanol and hexane atmosphere, the higher the pressure, the larger the number of molecules and carbon atoms around the electrodes. Therefore, an increase in the pressure increases the number of molecules which can be carbon sources. The pressure dependence of the yields supports our conclusion that the ambient carbons can be another source of carbon. In comparison, the yield was saturated above 400 Torr. In order to synthesize CNTs, we generated an arc discharge with constant current and voltage (100 A and 20 V) at various pressures. In other words, we introduced energy at a constant rate of 2 kW to the interelectrode space. The energy flow contributes to the synthesis of CNTs. The yield is restricted by the energy flow. In the case of constant energy flow, there would be maximum yield of MWNTs even though the pressure of the organic molecules is high.

We now discuss the effect of the molecular species on the synthesis. Ethanol, acetone and hexane have two, three, and six carbon atoms per molecule, respectively. This means that there are more carbon atoms around the electrodes in hexane than in ethanol atmospheres at the same pressure. Therefore, the number of carbon atoms included in the molecules can explain the order of the synthetic yields among the three molecules. This simple consideration also suggests that the presence of ambient carbons increases the yield of MWNTs. Therefore, we can conclude that ambient carbons, which originate from the organic molecules, increase the yield of MWNTs.

Finally, we consider the behavior of the organic molecules during discharge. The arc discharge has an arc plasma between the electrodes. In this plasma, He is not ionized because the ionization energy of He (24.6 eV) is larger than the kinetic energy of the electrons (~20 eV in our case). However, the ionization energy of a carbon atom (11.3 eV) is smaller than the kinetic energy of electrons. Therefore, carbon atoms can be ionized in the arc plasma [22]. Furthermore,

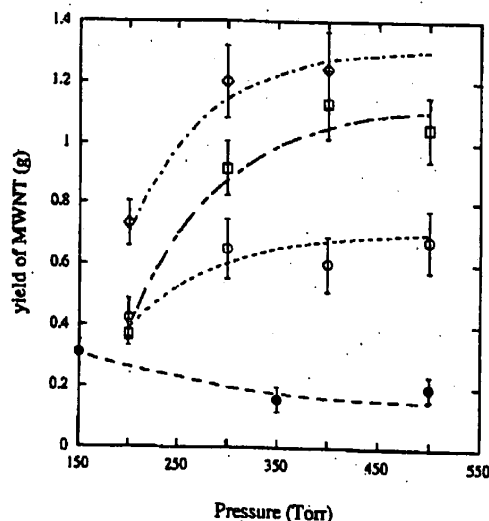


Fig. 4. Pressure dependence of yield of MWNTs: ●, helium; ○, ethanol; □, acetone; and ◇, hexane atmosphere. The yields are normalized by discharging time

the ionization energies of the three organic molecules are all about 10 eV. The bond energies of C-H and C-C are ~5 eV and ~9 eV, respectively, for the organic molecules. The ionization energy and the bond energy are smaller than the kinetic energy of the electrons. Therefore, acetone, ethanol and hexane can be ionized, and the molecules can be decomposed into hydrogen and carbon atoms. Furthermore, some of the decomposed atoms can also be ionized. These ionized species may contribute the synthesis of MWNTs. This needs further investigation.

3 Conclusions

We have modified the DC arc discharge method by introducing organic molecules during the discharging process. This allows us to synthesize about five times more MWNTs than are synthesized using the usual arc discharge method, using discharge conditions of 100 A and 20 V. We conclude that this increase in the yield of MWNTs can be attributed to the presence of ambient carbons.

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